Journal of Power Sources 238 (2013) 318–323

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Mechanical properties of Nafion 212 proton exchange membrane subjected to hygrothermal aging

Shouwen Shi, Gang Chen, Zhenfeng Wang, Xu Chen*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

HIGHLIGHTS

► The effect of hygrothermal aging on mechanical responses of PEM is investigated.
► Higher modulus and tensile strength are obtained for hygrothermal aging PEM.
► The effect of hygrothermal aging on the creep strain of PEM is quantitatively assessed.

ARTICLE INFO

Article history:
Received 24 December 2012
Received in revised form
7 March 2013
Accepted 10 March 2013
Available online 19 March 2013

Keywords:
Hygrothermal aging
Proton exchange membrane
Fuel cell
Mechanical responses

ABSTRACT

The effect of hygrothermal aging on proton exchange membrane (PEM) is a critical issue because the membrane is always subjected to high temperature and humidity under operation conditions. In this study, the mechanical responses of the Nafion 212 membrane subjected to hygrothermal aging are investigated experimentally through uniaxial tensile, stress relaxation and creep-recovery tests. Higher modulus and tensile strength are obtained for longer membrane aging because of the formation of crosslinks during the aging process. The creep strain is divided into three components to quantitatively assess the effect of hygrothermal aging on the mechanical responses of the membrane, and the predominant creep strain component changes as the hygrothermal aging time increases. In general, hygrothermal aging significantly affected the viscous flow strain and delayed elastic strain in correspondence to chain disentanglement and slippage, respectively. In addition, the effect of temperature on the creep behavior of the membrane aging for various times is also studied. The delayed elastic strain increases significantly as the aging time increases, while the instantaneous strain is least affected.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising technology as an alternative to traditional technologies utilizing fossil fuels. However, the widespread commercialization of this technology is hindered by both the expensive materials and the relatively low durability of proton exchange membrane (PEM) which cannot satisfy current requirements [1–6]. As a failure mode, pinhole formation is believed to be the contribution of build-up of stresses resulted from hygrothermal cycles during fuel cell operation [7–14]. Since the membrane is frequently subjected to high temperature and high humidity, which will inevitably result in significant changes of mechanical properties due to degradation or aging [15], therefore, special attention should be paid to it.

Traditionally, hygrothermal aging was considered to have an adverse effect on the mechanical performance of materials. Gao et al. [16] reported that the shear strength of anisotropic conductive adhesive joints decreased with increasing hygrothermal aging time. The same effect was also observed by Lin et al. [17]. The tensile properties of anisotropic conductive films were also investigated by Mei et al. [18], who concluded that the mechanical responses basically declined with the increase in hygrothermal aging time. However, the mechanical responses of PEM subjected to hygrothermal aging have not been thoroughly investigated yet. According to the prediction of Collette et al. based on infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) [19], the tensile strength of Nafion membrane would increase because the pendent chains are crosslinked. In addition, they also reported decreased water uptake and reduced conductivity ability. The effect of aging on the mechanical properties of the membrane was also examined by Uan-Zo-li [15], who conducted temperature scanning tests on Nafion membrane aged in deionized (DI) water and found that the glass transition temperature T_g increased with aging time. This increase was ascribed to the reduction of free volume upon aging. Uan-Zo-li also reported that changes in the membrane

* Corresponding author. Tel.: +86 22 27408399; fax: +86 22 27403389.
E-mail address: xchen@tju.edu.cn (X. Chen).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.03.042

structure upon aging were irreversible, while those of the virgin membrane were reversible. Patankar et al. [20] also investigated the physical aging effect on Nafion by constructing a time–aging master curve, and they observed higher moduli after aging. They attributed the high moduli to the formation of secondary crystalline, which acted as crosslinking sites for the rest of amorphous phase. After rejuvenating the membrane, the modulus recovered and was found to be consistent with that of the virgin membrane. The microstructural changes of the membrane during heating up and cooling down were examined by Kusoglu et al. [21] through small- and wide-angle X-ray scattering (SAXS and WAXS), providing an insight into the mechanical properties of the membrane. They noticed that a crystalline peak formed after cooling the membrane sample from 200 °C rather than heating up, explaining how annealing influenced the membrane's mechanical properties and water-uptake behavior. Other investigations concerning microstructure and its relationship with mechanical properties can also be found in the literature [22–27].

To our knowledge, the mechanical properties of proton exchange membrane subjected to hygrothermal aging have not been investigated thoroughly. An evaluation of the effect of hygrothermal aging on the mechanical properties of PEM will add fundamental understanding of the reliability of PEM under different operation conditions and help optimize the design of the next generation of membranes for fuel cell applications. Since the PEMFC typically operates at 85 °C, the aging environment in this study was set at 85 °C and 85% RH. The uniaxial tensile, stress relaxation and creep-recovery behaviors of membranes aged for different periods of time were investigated.

2. Experiments

Commercial Nafion®-212 membranes developed and manufactured by DuPont with a thickness of 50 μm were used in this study. Prior to testing, the specimens were put into a chamber maintained at a constant hygrothermal environment (85 °C and 85% RH), which served as an accelerator for the degradation of the membrane. The specimens were kept in the chamber for various times (24, 96, 168, 300, 500, and 1000 h) to investigate the effect of aging time on the mechanical responses of the membrane. The virgin membrane without aging was defined as aging for 0 h. Given that the specimens were films with one dimension much smaller than the other two, the membranes were hung in the chamber to ensure that all sides of the membranes were subjected to the hygrothermal environment. After aging, the specimens were then exposed to ambient conditions (25 °C, 60% RH) for 24 h.

The mechanical tests were conducted on a dynamic mechanical analysis (DMA-Q800, TA instruments) with a film tension clamp as shown in Fig. 1. Uniaxial tensile experiments were carried out on specimens aged for different periods of time at 85 °C and the strain rates of 0.001 s^{-1}, 0.01 s^{-1} and 0.08 s^{-1}. In addition, the creep-recovery and stress relaxation behaviors of the aged membranes were investigated at different temperatures. The stress relaxation tests were all conducted at 85 °C at a constant strain of 10%. In the creep-recovery experiments, the membrane was allowed to creep for 40 min under a steady stress of 2 MPa and recovered for 20 min without loading at the temperatures of 55 °C and 85 °C.

3. Results and discussion

3.1. Effect of strain rate

The stress–strain responses of the aged membranes subjected to uniaxial tensile loading under different strain rates are shown in Fig. 2. The stress–strain responses are rate dependent, implying the viscous nature of the membranes. As the strain rate increases, the yielding stress increases as well. Conspicuous yielding takes place in the membrane at the lower strain rate of 0.001 s^{-1}. With the increase of strain rate, the local maximum stress at the yield point disappears. The bundle-cluster model proposed by Liu et al. [28,29] was used to provide an insight into this phenomenon. This model was an development of the model proposed by Van der Heijden et al. [26] in that they all conceived that the bundles of aggregates rotate at lower strain rate while orient themselves within the

Fig. 1. Film tension clamp of DMA.

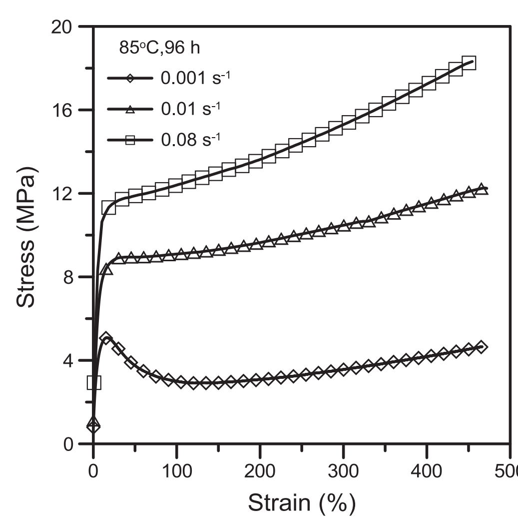

Fig. 2. Stress–strain response of membrane aged at 85 °C for 96 h under different strain rates.

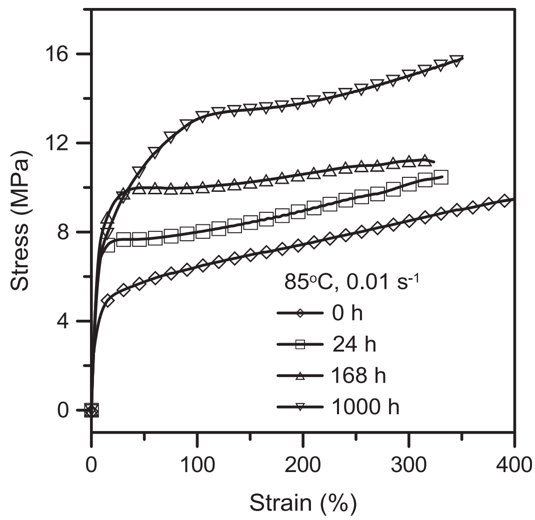

Fig. 3. Uniaxial tensile curves of membranes aged for different periods of time.

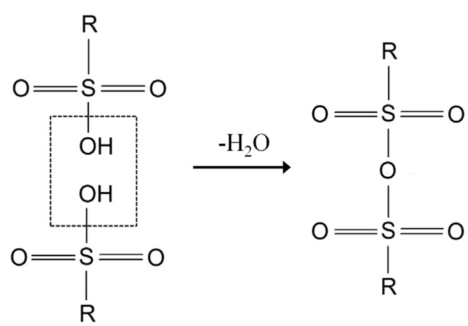

Fig. 4. Reaction of sulfonic acids condensation [19].

bundle at higher strain. The yielding point corresponds to the onset of disentanglement of polymer backbone chains. The faster the load is applied, the less time the polymer chains have to orient and change their relative positions. As a result, less free volume will be generated during the loading process, and the initial stress–strain region before yielding will be pushed higher without the onset of

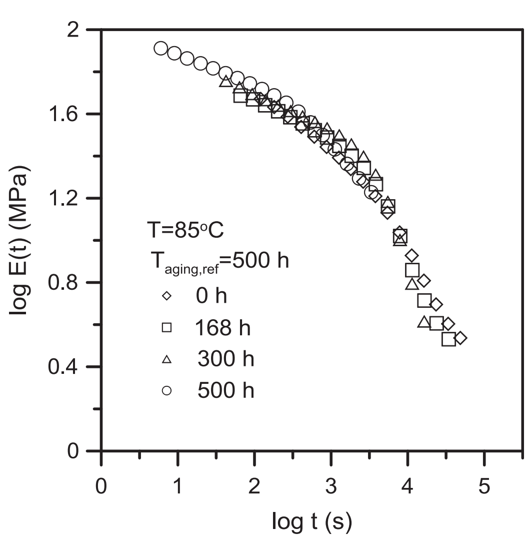

Fig. 5. Time–aging master curve for stress-relaxation modulus at 85 °C.

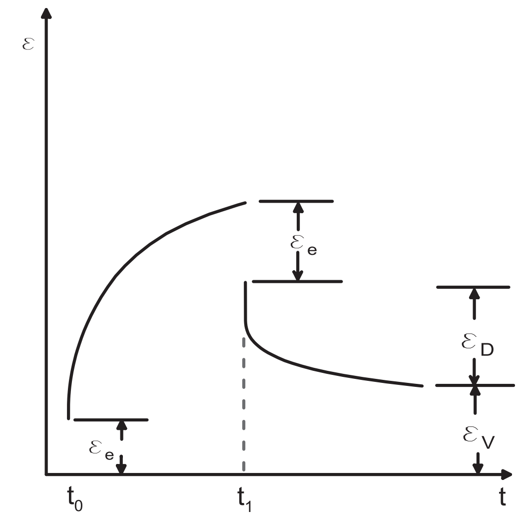

Fig. 6. Representation of typical creep-recovery curve and strain components.

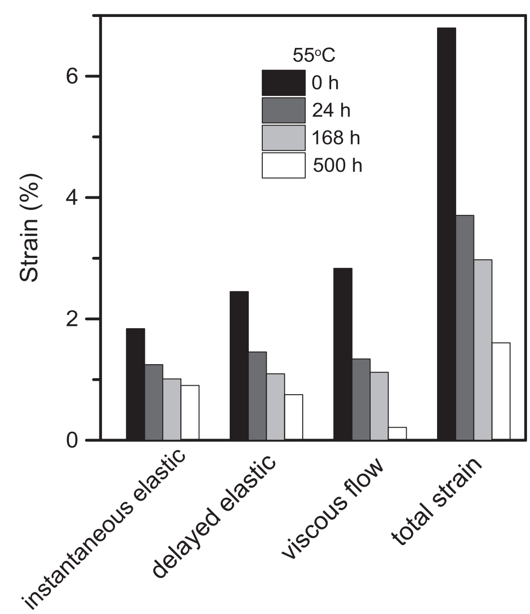

Fig. 7. Creep strain and components at 55 °C at different aging times.

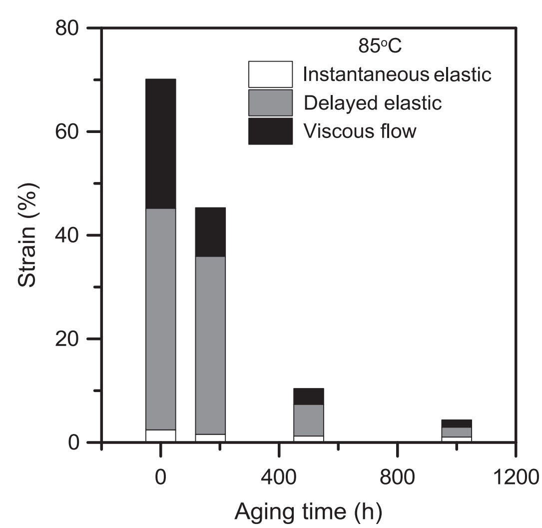

Fig. 8. Creep strain and components at 85 °C as a function of aging time.

disentanglement. Since the membrane has enough time to disentangle at low strain rates, more free volume will be obtained, and thus making the membrane more vulnerable to deformation.

3.2. Effect of aging time

The tensile properties of membranes with different hygrothermal aging times are shown in Fig. 3. Against the conventional wisdom that hygrothermal aging significantly reduces the strength of polymers, such as anisotropic conductive adhesive joints, the tensile strength of the membrane increases with the increase in aging time. This phenomenon is beneficial to the operation of the membrane at high humidities and high temperatures in terms of mechanical durability. However, this increase in tensile strength of the membrane is accompanied by a decrease in water uptake and ionic conductivity, as reported by Collette et al. [19], who performed a very long study (400 days) on membranes aged at 80 °C and 80% RH. The reduction in ionic conductivity and the increase in tensile strength were ascribed to the formation of sulfonic anhydride during aging [19]. The sulfonic anhydride is formed by the condensation of two sulfonic acids, creating a S–O–S crosslink between two side groups and accompanied by the loss of a water molecule, as shown in Fig. 4. Since the crosslink is formed between two adjacent side chains, the membrane becomes more resistant to deformation. Thus the tensile strength increases, as expected.

A time–aging master curve was constructed based on principal that is much like the well-known time-temperature superposition principle (TTSP) used to construct a hygrothermal master curve. A hygrothermal master curve can be formed by shifting the modulus data horizontally along the time axis, as the hygral and thermal shift factors are functions of humidity and temperature only; and vertically to account for the entropic and density changes [20]. Likewise, on constructing a time–aging master curve, the aging shift factor is a function of aging time. Fig. 5 shows the time–aging master curve constructed for the stress relaxation modulus at 85 °C. In consistence with the results of tensile loading, the membrane shows high modulus after aging for long periods. Aging acts as a stiffener because of the crosslinks produced during the aging

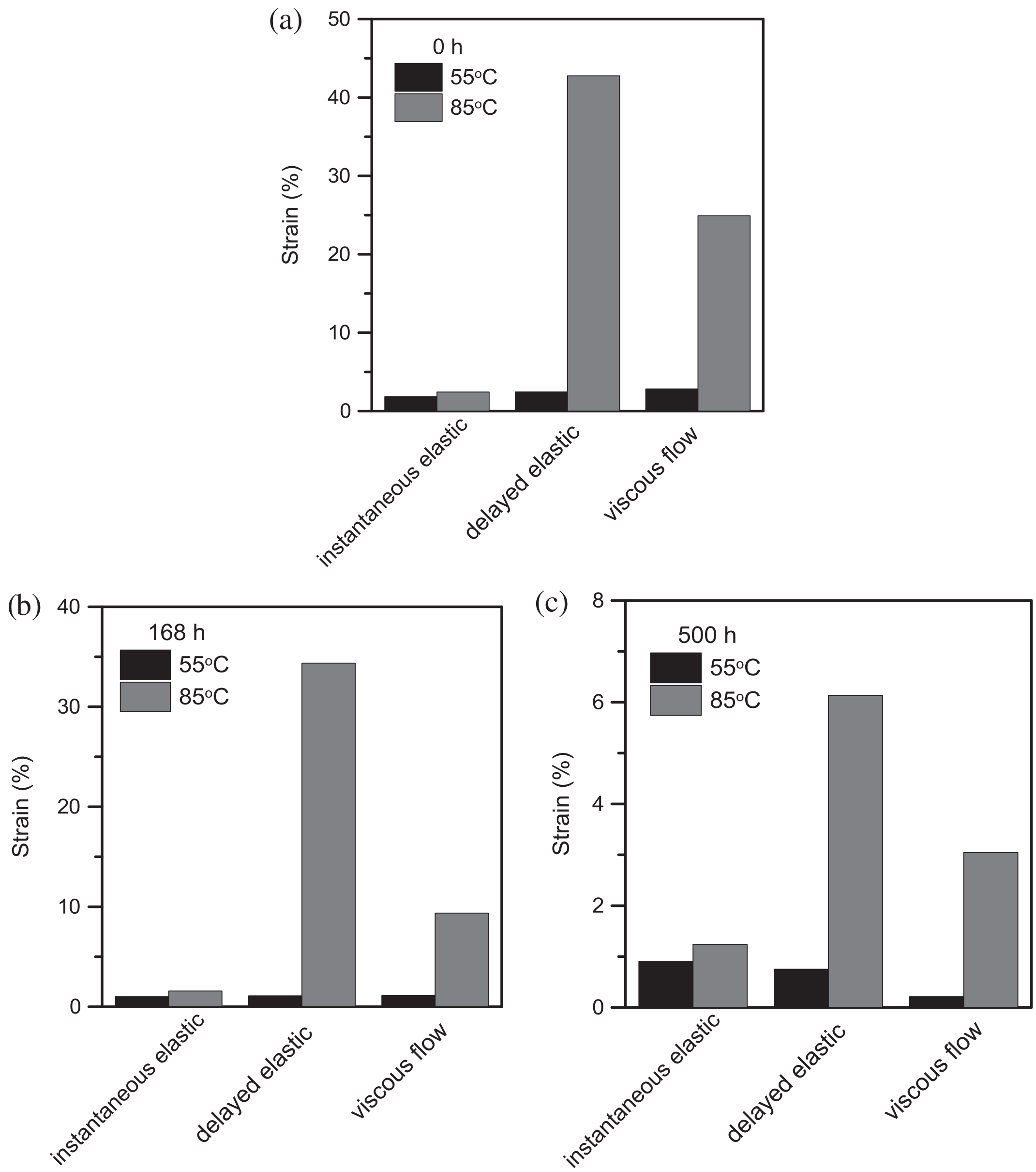

Fig. 9. Comparison of creep strain components at different temperatures for membranes aged for various periods of time: (a) 0 h; (b) 168 h; (c) 500 h.

process, and the longer the membrane subjected to aging, the stiffer the membrane was due to the fact that more and more crosslinks are formed with the increase in aging time. As reported by Patankar et al. [20] in dealing with dry-humidity transition using the time–temperature superposition principle (TTSP), the fact that data collected at humidity level below 5% RH did not superimpose with those collected at higher humidity levels suggested changes in mechanisms of mechanical behavior. Therefore, the hygrothermal master curve could be used as an indicator of the onset of changes in mechanisms. In this work, the master curve is generally smooth, and the curve for the virgin membrane superimposed with those for the aged membranes, implying that they almost have the same mechanism.

3.3. Tensile creep responses

The creep behavior of the membrane was investigated in order to explore the deformation mechanism from the mechanical perspective. In the approach of Majsztrik et al. [30], the creep strain can be viewed as a combination of individual strain components representing different molecular contributions, as shown in Fig. 6. The instantaneous elastic strain (ε_e) is an immediately, completely recoverable strain representing bond stretching/bending and crosslinking between chains. ε_D denotes the delayed elastic strain whose strain decreases with time and is completely recoverable. It refers to chain uncoiling. Viscous flow (ε_V), which is irrecoverable as determined from the strain at the end of creep-recovery tests, refers to chain slippage. One thing to be noted here is that the instantaneous elastic strain determined from the initial loading period is not always equal to that determined from the unloading period. This inequality is the result of the nonlinear behavior of the membrane, which is especially obvious at high temperatures and high strains, as discussed in our previous work [31]. However, this inequality did not have great impact on our study as long as we obtained the instantaneous elastic strain value using the same approach. Throughout this work, the instantaneous elastic strain was determined from the initial loading period.

The contributions of the components to creep strain as a function of aging time are shown in Figs. 7 and 8. All three components generally follow the same trend at both 55 and 85 °C that each strain component decreases with the increase of aging time, again suggesting the hardening effect of aging time, as we had discussed before. An in-depth analysis of each component for a certain aging time showed that different components predominated at different aging times. At 55 °C, the viscous flow component plays the leading role for membrane aging for 0 h. However, the leading role is taken over by the delayed elastic strain when the membrane is aged for 24 h. As the aging time increases to 168 h, all three components make almost the same contribution to the total strain. As the aging time increases to 500 h, the instantaneous elastic strain finally takes the leading position. Figs. 7 and 8 show that the aging time had the most significant effect on viscous flow strain but the least effect on instantaneous elastic strain. Taking into consideration of the representation of each strain component, we can conclude that hygrothermal aging hinders the uncoiling and slippage of chains. Since hygrothermal aging resulted in crosslinks, therefore, it is the crosslink that retard the evolution of creep strain, especially the delayed elastic strain and flow viscous strain. It is noteworthy that the total strain is not always equal to the sum of the individual components because of the nonlinearity of the membrane, as discussed above.

At 85 °C, all the creep components values decrease with the increase in aging time, the same as at 55 °C. However, within the range of aging times of our study, the dominant component at 85 °C is always the delayed elastic strain. Hence, the increase in temperature mainly serves to boost the delayed elastic strain. In other words, an increase in temperature provides the energy for chains to uncoil and disentangle. A detailed comparison to illustrate the effect of temperature on the evolution of each strain component is shown in Fig. 9. Creep strain components for membranes aging for different time (0, 168 and 500 h) are compared at two temperatures. For each membrane, the increase in delayed elastic strain is the most significant, but the increase in instantaneous elastic strain is relatively small, indicating that the increased energy increases the delayed elastic strain, not the instantaneous elastic strain because 85 °C is closer than 55 °C to the glass transition (~100 °C), at which the chain segments are susceptible to move, resulting in the disentanglement of chains.

4. Conclusions

The mechanical responses of Nafion 212 PEM aged for different periods of time under a hygrothermal environment are studied. Some important conclusions can be drawn as follows:

(1) The membrane remains rate-dependent after aging, and the yielding point of a tensile curve corresponds to the disentanglement of chains at the micro level. The modulus and tensile strength increases with the increase in aging time because of the formation of sulfonic anhydride, which acts as crosslinks during the aging process.
(2) An aging–time master curve for the stress-relaxation modulus is constructed, and the data for virgin membrane superimpose quite well with those for the aged membrane. The relaxation modulus increases with increasing membrane aging time for longer periods.
(3) Tensile creep property is investigated at different temperatures, and the creep strain is divided into three components in order to assess the deformation process quantitatively. At 55 °C, the type of component that takes the dominant role changes with aging time. For the virgin membrane, the viscous flow component predominates during creep, but the dominant role is taken over by the delayed elastic strain after aging for 24 h. Finally, after aging for 500 h, the instantaneous elastic strain becomes the dominant component of creep strain. Aging greatly retards the evolution of viscous flow strain.
(4) The effect of temperature on the creep evolution of membrane aged for various hours is investigated. The delayed elastic strain increases with increasing temperature, corresponding to the uncoiling of chains, but the instantaneous elastic strain is hardly affected.

Acknowledgments

The authors gratefully acknowledge financial support for this work from the Program of Introducing Talents of Discipline to Universities (No: B06006).

References

[1] Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, Appl. Energy 88 (2011) 981–1007.
[2] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, J. Power Sources 184 (2008) 104–119.
[3] R. Devanathan, Energy Environ. Sci. 1 (2008) 101–119.
[4] F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Fuel Cells 8 (2008) 3–22.
[5] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z.S. Liu, H. Wang, J. Shen, J. Power Sources 165 (2007) 739–756.
[6] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.I. Kimijima, N. Iwashita, Chem. Rev. 107 (2007) 3904–3951.

[7] Y.H. Lai, C.K. Mittelsteadt, C.S. Gittleman, D.A. Dillard, J. Fuel Cell Sci. Technol. 6 (2009) 021002–021014.
[8] Y. Lai, D. Dillard, Mechanical durability characterization and modeling of ionomeric membranes, in: W. Vielstich, H.A. Gaistager, H. Yokokawa (Eds.), Handbook of Fuel Cells: Advances in Electrocatalysis, Materials, Diagnostics and Durability, vol. 5, John Wiley and Sons, New York, 2009, pp. 403–419.
[9] K.A. Patankar, D.A. Dillard, S.W. Case, M.W. Ellis, Y.H. Lai, M.K. Budinski, C.S. Gittleman, Mech. Time-Depend. Mater. 12 (2008) 221–236.
[10] P.W. Majsztrik, Mechanical and Transport Properties of Nafion for PEM Fuel Cells: Temperature and Hydration Effects, Ph.D. Dissertation, Princeton University, Princeton, NJ, 2008.
[11] R. Solasi, Y. Zou, X. Huang, K. Reifsnider, D. Condit, J. Power Sources 167 (2007) 366–377.
[12] A. Kusoglu, A.M. Karlsson, M.H. Santare, S. Cleghorn, W.B. Johnson, J. Power Sources 170 (2007) 345–358.
[13] Y. Tang, A.M. Karlsson, M.H. Santare, M. Gilbert, S. Cleghorn, W.B. Johnson, Mater. Sci. Eng., A 425 (2006) 297–304.
[14] A. Kusoglu, A.M. Karlsson, M.H. Santare, S. Cleghorn, W.B. Johnson, J. Power Sources 161 (2006) 987–996.
[15] J.T. Uan-Zo-li, The Effects of Structure, Humidity and Aging on the Mechanical Properties of Polymeric Ionomers for Fuel Cell Applications, Master Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, 2001.
[16] L.L. Gao, X. Chen, H. Gao, Int. J. Adhes. Adhes. 33 (2012) 75–79.
[17] Y. Lin, X. Chen, Z. Wang, J. Adhes. Sci. Technol. 20 (2006) 1383–1399.
[18] Y. Mei, X. Chen, H. Gao, J. Electron. Mater. 38 (2009) 2415–2426.
[19] F.M. Collette, C. Lorentz, G. Gebel, F. Thominette, J. Membr. Sci. 330 (2009) 21–29.
[20] K. Patankar, D. Dillard, S. Case, M. Ellis, Y.H. Lai, C. Gittleman, Fuel Cells 12 (2012) 787–799.
[21] A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, Macromolecules 45 (2012) 7467–7476.
[22] J. Li, J.K. Park, R.B. Moore, L.A. Madsen, Nat. Mater. 10 (2011) 507–511.
[23] O. Diat, G. Gebel, Nat. Mater. 7 (2008) 13–14.
[24] K. Schmidt-Rohr, Q. Chen, Nat. Mater. 7 (2007) 75–83.
[25] G. Gebel, O. Diat, Fuel Cells 5 (2005) 261–276.
[26] P. Van der Heijden, L. Rubatat, O. Diat, Macromolecules 37 (2004) 5327–5336.
[27] L. Rubatat, G. Gebel, O. Diat, Macromolecules 37 (2004) 7772–7783.
[28] D. Liu, S. Kyriakides, S.W. Case, J.J. Lesko, Y. Li, J.E. McGrath, J. Polym. Sci., Part B: Polym. Phys. 44 (2006) 1453–1465.
[29] D. Liu, M.A. Hickner, S.W. Case, J.J. Lesko, J. Eng. Mater. Technol.-Trans. ASME 128 (2006) 503–508.
[30] P.W. Majsztrik, A.B. Bocarsly, J.B. Benziger, Macromolecules 41 (2008) 9849–9862.
[31] S. Shi, D. Yu, G. Chen, J. Chen, X. Chen, J. Power Sources 213 (2012) 40–46.